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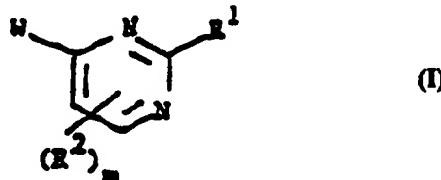
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(54) Title: HERBICIDAL ARYL AND HETEROARYL PYRIMIDINES

(57) Abstract

This invention relates to novel aryl and heteroaryl pyrimidine derivatives, shown below, substituted at the 2- and 4-position of the pyrimidine ring, their use as herbicides and agricultural compositions comprising the same. In formula (I), W is a substituted phenyl or a substituted 5- or 6-membered aromatic heterocyclic ring wherein one or two atoms of said ring are selected from oxygen, nitrogen and sulfur; W being substituted by at least R; R is  $\text{CO}_2\text{R}^4$ ,  $\text{CHO}$ ,  $\text{CONH-O-CH}_2\text{CO}_2\text{R}^4$ ,  $\text{COSR}^4$ ,  $\text{CO}_2\text{CHR}^5\text{OCOR}^6$  or  $\text{CH=NOR}^4$ ;  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$  are as defined in the application; m = 1 or 2.



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## HERBICIDAL ARYL AND HETEROARYL PYRIMIDINES

### BACKGROUND OF THE INVENTION

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This invention relates to novel substituted aryl and heteroaryl pyrimidines, their use as herbicides and agricultural compositions comprising the same.

Various pesticidal aryl and heteroaryl pyrimidines are known. U.S. Patent No. 10 4,752,324 discloses 2-(2-alkyl-6-arylpyrimidin-4-yl)nicotinic acid derivatives having herbicidal activity. DE 40 31 798 describes fungicidal substituted pyridylpyrimidines. Furthermore, Harris et al. Aust. J. Chem., 1979, 32, 669-679, describes the plant growth regulating properties of diaryl heterocyclic compounds.

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### DESCRIPTION OF THE INVENTION

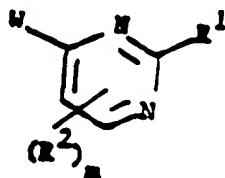
It has now been discovered that certain aryl and heteroaryl pyrimidines substituted at the 2 and 4-position of the pyrimidine ring exhibit herbicidal and plant growth regulating activity, when applied either pre or post emergence and used against annual and 20 perennial grasses and broad leaf weeds.

The terms "herbicide" and "herbicidal" are used herein to denote the inhibitive control or modification of undesired plant growth. Inhibitive control and modification include all deviations from natural development such as, for example, total killing, growth 25 retardation, defoliation, desiccation, regulation, stunting, tillering, stimulation, leaf burn, and dwarfing. The term "herbically effective amount" is used to denote any amount which achieves such control or modification when applied to the undesired plants themselves or to the area in which these plants are growing. The term "plants" is intended to include germinant seeds, emerging seedlings and established vegetation, including both 30 roots and above-ground portions.

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More particularly, this invention concerns compounds of the general formula I.

5



I

wherein W is a substituted phenyl or a substituted 5- or 6-membered aromatic heterocyclic ring wherein one or two atoms of said ring are selected from oxygen, nitrogen and sulfur;

10 W being substituted by at least R;

R is  $\text{CO}_2\text{R}^4$ ,  $\text{CHO}$ ,  $\text{CONH-O-CH}_2\text{CO}_2\text{R}^4$ ,  $\text{COSR}^4$ ,  $\text{CO}_2\text{CHR}^5\text{OCOR}^6$  or  $\text{CH=N-OR}^4$ ;

15 R<sup>1</sup> is Ar, (Z), Y-Ar, or ZAr wherein Ar is an optionally substituted aryl or heteroaryl group selected from the group consisting of phenyl, pyridyl, piperonyl, naphthyl, indolyl, quinolyl, isoquinolyl, quinoxaliny, quinazolinyl, benzoxazolyl, benzothiazolyl, phenanthryl, pyridyl-N-oxide, anthranilyl, pyrimidinyl, pyrazinyl, thieryl, furyl, pyrrolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, imidazolyl, pyrazolyl, oxadiazolyl and

20 thiadiazolyl wherein the optional substituents are phenoxy, halo, alkyl, alkenyl, haloalkyl, haloalkylthio, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, haloalkoxy, alkoxyalkyl, cyano, nitro, alkoxycarbonyl, amino, alkylamino, dialkylamino, hydroxy, Y is O, S or NH; Z is an optionally substituted C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>2</sub>-C<sub>4</sub>alkynyl or an optionally substituted C<sub>2</sub>-C<sub>4</sub>alkenyl, wherein the substituents are independently alkyl and halogen, x is 0 to 2;

25

R<sup>2</sup> is independently hydrogen, halogen, alkyl, alkenyl, haloalkyl, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, alkoxyalkyl, cyano, nitro, amino, alkylamino, dialkylamino,  $\text{CO}_2\text{R}^4$  and hydroxy, m is 1 to 2;

30 R<sup>4</sup> is hydrogen, alkali or alkaline earth cation, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium

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cation, trialkylsulfoxonium cation, alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl;

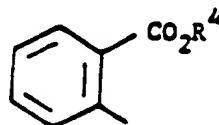
R<sup>5</sup> is hydrogen or alkyl; and

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R<sup>6</sup> is alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl;

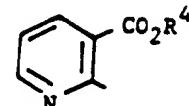
provided that (i) when R<sup>1</sup> is phenyl; W is not

10



and (ii) when R<sup>1</sup> is optionally substituted phenyl and W is

15 R<sup>2</sup> is not alkyl or alkenyl.



The term "alkyl" as used herein includes straight, branched and cyclo alkyl groups, preferably containing up to 6 carbon atoms. This applies to alkyl moieties contained for example, in "haloalkyl" and each alkyl group of "alkoxyalkyl". The term "alkenyl" is  
20 represented by 2 to 6 carbon atoms.

Suitable halogen groups include fluorine, chlorine, bromine, and iodine. Haloalkyl groups may be substituted by one or more halogen atoms. The term "alkali cation" is defined as metals of group 1A of the periodic chart and particularly include sodium and  
25 potassium. The term "alkaline earth cation" includes magnesium, calcium, strontium and barium.

The term "phenylalkyl" refers to an alkyl group substituted with a phenyl. The terms "optionally substituted phenyl", "optionally substituted phenylalkyl" and "optionally  
30 substituted phenoxy" refers to a phenyl, phenylalkyl, or phenoxy group substituted at one or more of the ring carbon atoms with a group selected from alkyl, haloalkyl, halogen,

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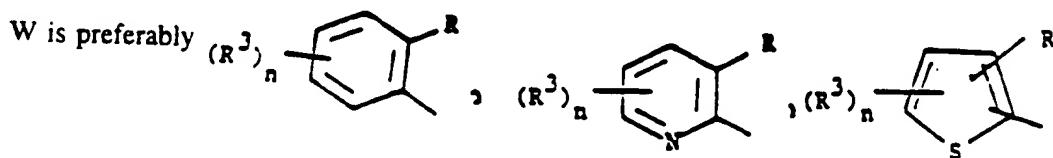
alkoxy, alkenyl, cyano, and nitro.

The term "substituted ammonium cation" refers to an ammonium cation substituted by a  $C_1$ - $C_{20}$ alkyl, di- $C_1$ - $C_{20}$ alkyl, tri- $C_1$ - $C_{20}$ alkyl, tetra- $C_1$ - $C_{20}$ alkyl, hydroxy- $C_1$ - $C_5$ alkyl, 5 di(hydroxy- $C_1$ - $C_5$ alkyl), tri(hydroxy- $C_1$ - $C_5$ alkyl),  $C_1$ ,alkoxy- $C_1$ - $C_5$ alkyl, hydroxy- $C_1$ - $C_5$ alkoxy- $C_1$ - $C_5$ alkyl or  $C_1$ - $C_5$ alkoxycarbonyl- $C_1$ - $C_5$ alkyl group.

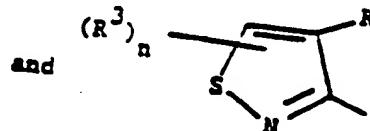
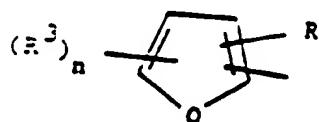
A preferred sub-group of compounds of formula I are compounds wherein W is phenyl, pyridyl, thienyl, furyl or isothiazolyl.

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W is preferably



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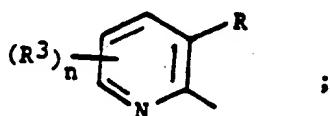
wherein  $R^3$  is independently hydrogen, halogen, alkyl, haloalkyl, alkoxy, cyano, alkoxy carbonyl, alkylamino, dialkylamino and  $-N(R^5)-CO-R^6$ , and n is 1 to 4.

20

A particularly preferred subgroup of compounds of formula I are compounds wherein

25

(i) W is



(ii) R is  $CO_2R^4$ ,  $CHO$ ,  $CONH-O-CH_2CO_2R^4$ ,  $COSR^4$ ,  $CO_2CHR^5OCOR^6$  or  $CH=NOR^4$ ;

30

(iii)  $R^1$  is Ar,  $(Z)_xYAr$  or  $ZAr$  wherein Ar is an optionally substituted phenyl,

pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl, anthranilyl or phenanthryl; Y is O, S or NH; Z is an optionally substituted C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>2</sub>-C<sub>4</sub>alkynyl or optionally substituted C<sub>2</sub>-C<sub>4</sub>alkenyl wherein the substituents are independently alkyl and halogen and x is 0 to 2;

5

(iv) R<sup>2</sup> is hydrogen, CO<sub>2</sub>R<sup>4</sup> and alkoxy;

(v) R<sup>3</sup> is hydrogen and halogen.

10 (vi) R<sup>4</sup> is hydrogen, alkali or alkaline earth cation, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium cation, trialkylsulfoxonium cation, alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl;

15 (vii) R<sup>5</sup> is hydrogen or alkyl; and

(viii) R<sup>6</sup> is alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl.

20 Preferably R is CO<sub>2</sub>CHR<sup>5</sup>OCOR<sup>6</sup> or CO<sub>2</sub>R<sup>4</sup> wherein R<sup>4</sup> is hydrogen, alkyl, alkali or alkaline earth cations, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium cation, or trialkyl sulfoxonium cation and

25 R<sup>1</sup> is optionally substituted phenyl, pyridyl, naphthyl, quinolyl, piperonyl, (Z)<sub>x</sub>Ophenyl and (Z)phenyl wherein Z is C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>2</sub>-C<sub>4</sub>alkynyl or C<sub>2</sub>-C<sub>4</sub>alkenyl and x is 1.

More prefreably R is CO<sub>2</sub>R<sup>4</sup> wherein R<sup>4</sup> is hydrogen, Na, NH<sub>4</sub>, K, Ca, Mg,  
30 trimethyl sulfonium, trimethyl sulfoxonium and isopropyl ammonium; and

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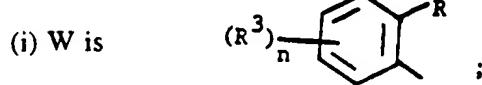
$R^1$  is phenyl or substituted phenyl wherein the substituents are independently methyl, methoxy, chloro, fluoro, amino, haloalkoxy, nitro and haloalkyl; and

$R^2$  is hydrogen, alkoxy, or  $CO_2R^4$ .

5.

Another particularly preferred subgroup of compounds of formula I are compounds wherein

10



(ii) R is  $CO_2R^4$ ,  $CHO$ ,  $CONH-O-CH_2CO_2R^4$ ,  $COSR^4$ ,  $CO_2CHR^5OCOR^6$  or  $CH=NOR^4$ ;

15

(iii)  $R^1$  is Ar,  $(Z)_xYAr$  or  $ZAr$  wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl, anthranilyl or phenanthryl; Y is O, S or NH; Z is an optionally substituted  $C_1-C_3$ alkyl,  $C_2-C_4$ alkynyl or optionally substituted  $C_2-C_4$ alkenyl wherein the substituents are independently alkyl and halogen and x is 0 to 2;

20

(iv)  $R^2$  is hydrogen,  $CO_2R^4$ , alkoxy and alkyl;

(v)  $R^3$  is hydrogen and halogen and n is 1 or 2;

25

(vi)  $R^4$  is hydrogen, alkali or alkaline earth cation, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium cation, trialkylsulfoxonium cation, alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl;

30

(vii)  $R^5$  is hydrogen or alkyl; and

(viii) R<sup>6</sup> is alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl.

5 Preferably R is CO<sub>2</sub>CHR<sup>5</sup>OCOR<sup>6</sup> or CO<sub>2</sub>R<sup>4</sup> wherein R<sup>4</sup> is hydrogen, alkyl, alkali or alkaline earth cations, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium cation, or trialkyl sulfoxonium cation and

10 R<sup>1</sup> is optionally substituted phenyl, pyridyl, naphthyl, quinolyl, piperonyl, (Z)<sub>x</sub>phenyl and (Z)phenyl wherein Z is C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>2</sub>-C<sub>4</sub>alkynyl or C<sub>2</sub>-C<sub>4</sub>alkenyl and x is 1.

More preferably R is CO<sub>2</sub>R<sup>4</sup> wherein R<sup>4</sup> is hydrogen, Na, NH<sub>4</sub>, K, Ca, Mg,

15 trimethyl sulfonium, trimethyl sulfoxonium and isopropyl ammonium; and

R<sup>1</sup> is phenyl or substituted phenyl wherein the substituents are independently methyl, methoxy, chloro, fluoro, amino, haloalkoxy, nitro and haloalkyl and R<sup>3</sup> is halogen.

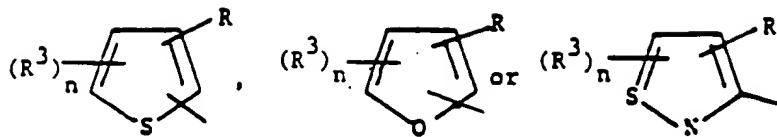
20 Another preferred sub group of compounds of Formula I include the compounds wherein R is CO<sub>2</sub>R<sup>4</sup>; R<sup>4</sup> is hydrogen, Na, NH<sub>4</sub>, K, Ca, Mg, trimethylsulfonium, trimethylsulfoxonium or isopropylammonium; R<sup>1</sup> is Ar, (Z)<sub>x</sub>Y-Ar and ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl or phenanthryl wherein the optional substituents are halo, alkyl, alkenyl, haloalkyl, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, haloalkoxy, alkoxyalkyl, cyano, nitro, alkoxycarbonyl, amino, alkylamino, dialkylamino and hydroxy;

25 Y is O, S or NH, preferably O; Z is an optionally substituted C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>2</sub>-C<sub>4</sub>alkynyl or an optionally substituted C<sub>2</sub>-C<sub>4</sub>alkenyl wherein the substituents are independently alkyl and halogen; and x is 0 to 2.

30 Still another preferred subgroup of compounds of Formula I include the compounds

wherein W is

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R is  $\text{CO}_2\text{R}^4$ ;  $\text{CHO}$ ;  $\text{CONH-O-CH}_2\text{CO}_2\text{R}^4$ ;  $\text{COSR}^4$ ;  $\text{CO}_2\text{CHR}^5\text{OCOR}^6$  or  $\text{CH=NOR}^4$ ;

$\text{R}^1$  is Ar,  $\text{Z}_1\text{OAr}$  or  $\text{ZAr}$  wherein Ar is an optionally substituted phenyl, pyridyl,  
10 naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl or phenanthryl;

$\text{R}^2$  is hydrogen; and

$\text{R}^3$  is hydrogen and halogen.

15

In another embodiment the invention includes a herbicidal composition comprising a herbicidally effective amount of a compound of Claim 1 in association with an agriculturally acceptable diluent.

20 A general process for making the compounds of this invention is as follows.

Appropriately substituted 1-(aryl or heteroaryl)-3-(N,N-dimethylamino)prop-2-en-1-one is heated with an appropriately substituted amidine or amidine hydrochloride and a (optional) base, such as sodium methoxide, in a suitable solvent, such as methanol, to  
25 afford the substituted 4-(aryl or heteroaryl)pyrimidine.

The substituted amidines used in this process were either purchased or prepared from commercially available starting materials. For example, the procedure of R.S.Garigipati (*Tetrahedron Letters*, 31, 1969 (1990)) was used to prepare amidines from  
30 the appropriately substituted nitrile by reaction with chloromethylaluminum amide in toluene.

The process for making the compounds of this invention will be more fully understood by reference to the following examples.

### EXAMPLE 1

5 a) Preparation of 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one.

A suspension of 27.1 g (164 mmol) 2-acetylpyridine-3-carboxylic acid in 200 mL toluene is heated to reflux to remove water by azeotropic distillation. After approximately 10 20 mL of distillate is collected, the solution is cooled to ambient temperature and 54 mL N,N-dimethylformamide dimethylacetal is added dropwise. The brown solution is heated to reflux for 5 h, allowed to cool and concentrated to low volume *in vacuo*. This solution is treated with diethyl ether and stirred overnight. The orange crystals (mp 126-129°C) are collected by vacuum filtration. The <sup>1</sup>H NMR and mass spectra are consistent with 1-15 (3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one.

b) Preparation of 2-[4-(2-phenyl)pyrimidinyl]-3-pyridinecarboxylic acid (Compound 7 in Table 1).

20 To a solution of 2.00 g (8.54 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one and 1.50 g (8.54 mmol) benzimidine hydrochloride hydrate in 100 mL anhydrous methanol, is added 4.0 mL 25% sodium methoxide in methanol. The resulting dark solution is refluxed for 6 h allowing about half of the methanol to distill off, then stirred at ambient temperature for 72 h and evaporated to 25 dryness *in vacuo*. The residue is partitioned between ethyl acetate and 0.5 M aqueous sodium hydroxide. The aqueous layer is washed once with ethyl acetate and acidified to pH 3 with concentrated HCl. The solid precipitate is collected by vacuum filtration and dried *in vacuo* at 50°C for 1 h to yield a tan solid, m.p. 169-170°C. The <sup>1</sup>H NMR and mass spectra are consistent with the desired 2-[4-(2-phenyl)pyrimidinyl]-3-pyridine-30 carboxylic acid.

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c) Preparation of 2-[4-(2-phenyl)pyrimidinyl]-3-pyridinecarboxylic acid, monosodium salt (Compound 1 in Table 1).

To a slurry of 1.00 g (3.61 mmol) 2-[4-(2-phenyl)pyrimidinyl]-3-pyridinecarboxylic acid in 10 mL methanol, is added 0.82 mL (3.61 mmol) 25% sodium methoxide in methanol. The solution is stirred for 5 min and evaporated *in vacuo* to yield a solid foam. The <sup>1</sup>H NMR and mass spectra are consistent with the 2-[4-(2-phenyl)pyrimidinyl]-3-pyridinecarboxylic acid, monosodium salt.

10

EXAMPLE 2

a) Preparation of 2-[4-[2-(3-chlorophenyl)]pyrimidinyl]-3-pyridinecarboxylic acid (Compound 14 in Table 1).

15 To a solution of 4.29 g (18.32 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one and 3.50 g (18.32 mmol) 3-chlorobenzamidine hydrochloride in 150 mL methanol, is added 8.5 mL 25% sodium methoxide in methanol. The resulting brown solution is refluxed for approximately 6 h allowing about half of the methanol to distill off, then allowed to cool, and evaporated *in vacuo*. The residue is  
20 partitioned between water and ethyl acetate. An insoluble solid is collected by vacuum filtration. This solid is dissolved in 1 M aqueous sodium hydroxide and acidified to pH 3 with concentrated HCl. The resulting precipitate is collected by vacuum filtration and dried to yield a tan solid (mp 163-166°C). The <sup>1</sup>H NMR and mass spectra are consistent with those expected for 2-[4-[2-(3-chlorophenyl)]pyrimidinyl]-3-pyridinecarboxylic acid.

25

EXAMPLE 3

Preparation of 2-[4-[2-(4-fluorophenyl)]pyrimidinyl]-3-pyridinecarboxylic acid (Compound 16 in Table 1).

30

To a solution of 5.88 g (25.1 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-

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dimethylamino)prop-2-en-1-one and 3.47 g (25.1 mmol) 4-fluorobenzamidine in 150 mL methanol is added 12.1 mL (53 mmol) 25% sodium methoxide in methanol. The solution is stirred and heated to reflux allowing some of the methanol to distill off. After 2 hours, the heat is turned off and the reaction is stirred at room temperature overnight.

5

The solution is refluxed for another 4 hours with removal of the distillate. The reaction is cooled and evaporated *in vacuo*. The residue is taken up in water and washed twice with ethyl acetate. A solid precipitate is formed in the ethyl acetate wash and collected by vacuum filtration. The solid is dissolved in 1 M NaOH, and acidified with 10 concentrated HCl. The resulting solid is collected by vacuum filtration. After drying *in vacuo*, a white solid is obtained (m.p. 194-196°C).

15 The original aqueous layer is acidified with concentrated HCl and the solid is collected by vacuum filtration. This solid is recrystallized from ethyl acetate to afford light tan crystals (m.p. 195-196°C). The <sup>1</sup>H NMR and mass spectra of both solids are identical and consistent with the desired 2-[4-[2-(4-fluorophenyl)]pyrimidinyl]-3-pyridinecarboxylic acid.

#### EXAMPLE 4

20

Preparation of 2-[4-[2-(3-chloro-4-methylphenyl)]pyrimidinyl]-3-pyridinecarboxylic acid (Compound 24 in Table 1).

To a solution of 3.47 g (14.8 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-di-25 methylamino)prop-2-en-1-one and 2.50 g (14.8 mmol) 3-chloro-4-methylbenzamidine in 150 mL methanol, is added 6.8 mL 25% sodium methoxide in methanol. The resulting solution is refluxed for 2 hours allowing about half of the methanol to distill off and stirred at ambient temperature over a weekend. Refluxing is continued for 4 additional hours, the mixture is cooled and evaporated *in vacuo*. The residue is treated with 1 M 30 aqueous sodium hydroxide and filtered to remove an insoluble solid. The filtrate is washed with ethyl acetate, acidified to pH 3 with concentrated HCl, and extracted with 3

portions of ethyl acetate, which upon evaporation *in vacuo*, afforded a tan solid. The insoluble solid obtained from the initial filtration is suspended in 1 M aqueous sodium hydroxide at 50°C until dissolution, washed with ethyl acetate, filtered, and acidified with concentrated HCl. The resulting aqueous solution is extracted with 2 portions of ethyl acetate. The ethyl acetate extracts are washed with water, dried over magnesium sulfate, filtered, and evaporated *in vacuo* to give a light tan solid, which is combined with the 0.20 g of tan solid obtained above. The <sup>1</sup>H NMR and mass spectra of this combination (mp 168-172°C) are consistent with the desired 2-[4-[2-(3-chloro-4-methylphenyl)]pyrimidinyl]-3-pyridinecarboxylic acid.

10

#### EXAMPLE 5

Preparation of 2-[4-[2-(3-chlorophenoxy)methyl]pyrimidinyl]-3-pyridinecarboxylic acid  
(Compound 22 in Table 1).

15

To a solution of 2.66 g (11.4 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one and 2.10 g (11.4 mmol) 3-chlorophenoxyacetamide in 100 mL methanol, is added 5.2 mL (22.8 mmol) 25% sodium methoxide in methanol. The resulting solution is gently refluxed overnight allowing about half of the methanol to distill off. The reaction mixture is evaporated *in vacuo* and the residue is partitioned between 0.5 M aqueous sodium hydroxide and ethyl acetate. The aqueous layer is washed with ethyl acetate, then acidified to pH 3 with concentrated HCl. The crude solid product is collected by vacuum filtration and purified by silica gel chromatography (2:1 ethyl acetate: methanol) to afford a tan solid (mp 155-158°C). The <sup>1</sup>H NMR and mass spectra of this solid are as expected for 2-[4-[2-(3-chlorophenoxy)methyl]pyrimidinyl]-3-pyridinecarboxylic acid.

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### EXAMPLE 6

Preparation of 2-[4-[2-(2-Phenyl)ethenyl]pyrimidine]-3-pyridinecarboxylic acid (Compound 26 in Table 1).

5

To a solution of 2.72 g (11.6 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one and 1.86 g (11.6 mmol) cinnamamidine in 50 mL methanol, is added 8.0 mL 25% sodium methoxide in methanol. The resulting dark solution is refluxed for 2 hours with removal of the distillate. After stirring at ambient 10 temperature for 72 hours, the reaction mixture is treated with 2.0 mL acetic acid and evaporated to dryness *in vacuo*. The residue is partitioned between saturated aqueous sodium bicarbonate and ethyl acetate. The aqueous layer is washed with two portions of ethyl acetate, acidified to pH 4 with concentrated HCl and filtered to remove crude solid product. The filtrate is extracted with ethyl acetate and evaporated *in vacuo* to yield a 15 brown oil. The crude solid is combined with the brown oil and purified by thin layer preparatory chromatography on silica gel with 180:20:1 dichloromethane: methanol:acetic acid to afford a tan solid (mp 167°C decomposition). The <sup>1</sup>H NMR spectrum of this solid is as expected for 2-[4-[2-(2-phenyl)ethenyl]pyrimidinyl]-3-pyridinecarboxylic acid.

20

### EXAMPLE 7

Preparation of 2-[4-[2-(1-naphthyl)]pyrimidinyl]-3-pyridinecarboxylic acid (Compound 27 in Table 1).

25

To a solution of 4.46 g (19 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-di-methylamino)prop-2-en-1-one and 3.24 g (19 mmol) 1-naphthamidine in 50 mL methanol, is added 13 mL (57 mmol) 25% sodium methoxide in methanol. The resulting dark solution is refluxed for 18 hours. The reaction mixture is treated with 3.3 mL acetic acid and evaporated *in vacuo*. The residue is chromatographed on silica gel with 4:1 ethyl 30 acetate:methanol. The product containing fractions are evaporated *in vacuo*, suspended in ethyl acetate, filtered and evaporated *in vacuo* to yield slightly impure product. This solid

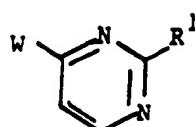
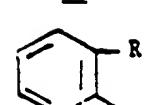
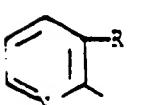
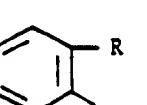
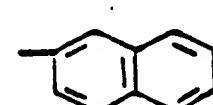
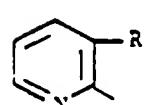
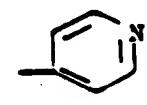
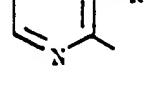
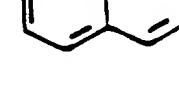
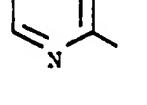
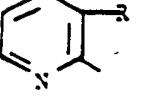
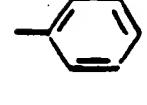
-14-

is rechromatographed on silica gel with 90:10:1 ethyl acetate:methanol:acetic acid to finally afford a tan solid (mp 205-207°C). The <sup>1</sup>H NMR spectrum of this solid is as expected for 2-[4-[2-(1-naphthyl)]-pyrimidinyl]-3pyridinecarboxylic acid.

5 These and other compounds which can be made by the foregoing processes are set forth in Tables 1 and 2 which follow, wherein the various substituent groups are indicated.

-15-

TABLE 1

5				
Cpd #	W	R	R'	m.p. °C
10		-CO <sub>2</sub> Na <sup>+</sup>		>270
15		CO <sub>2</sub> H		192.5-196
20		CO <sub>2</sub> Na <sup>+</sup>		260 (decomp.)
25		CO <sub>2</sub> H		287-289
30		CO <sub>2</sub> Na <sup>+</sup>		125 (decomp.)
35		CO <sub>2</sub> Na <sup>+</sup>		284 (decomp.)
40		CO <sub>2</sub> H		169-170

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TABLE 1 (cont)

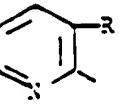
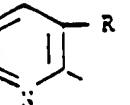
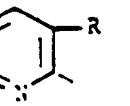
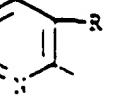
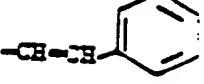
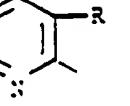
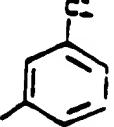
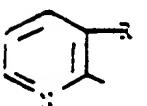
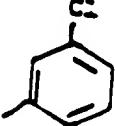
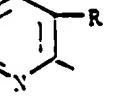
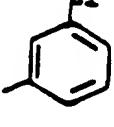
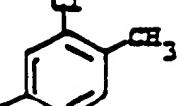
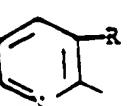
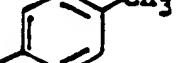
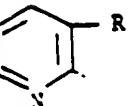
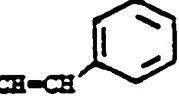
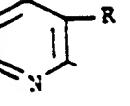
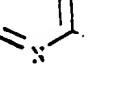
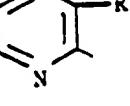
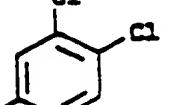
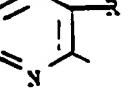
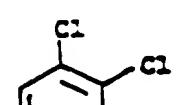
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5 8		$\text{CO}_2\text{Na}^+$		>270
10 9		$-\text{C}(=\text{O})-\text{NH}-\text{OCH}_2\text{CO}_2\text{CH}_3$		134-140.5
10 10		$\text{CO}_2\text{H}$		185 (decomp.)
15 11		$\text{CO}_2\text{Na}^+$		>300
20 12		$\text{CO}_2\text{Na}^+$		265 (decomp.)
25 13		$\text{CO}_2\text{CH}_3$		118-119
30 14		$\text{CO}_2\text{H}$		163-166
15		$\text{CO}_2\text{Na}^+$		>280

TABLE 1 (cont)

<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p. °C</u>
5 16		CO <sub>2</sub> H		195-196
17		CO <sub>2</sub> Na <sup>+</sup>		>280
10 18		CO <sub>2</sub> H		160-163
15 19		CO <sub>2</sub> Na <sup>+</sup>		64.5-123.5
20 21		CO <sub>2</sub> H		235-237 (decomp.)
20 21		CO <sub>2</sub> Na <sup>+</sup>		282 (decomp.)
25 22		CO <sub>2</sub> H		155-158
30 23		CO <sub>2</sub> Na <sup>+</sup>		245-251

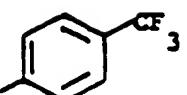
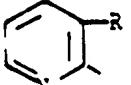
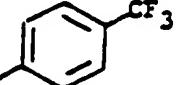
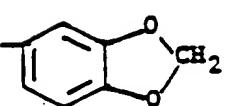
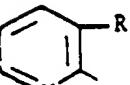
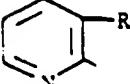
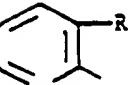
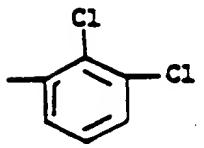
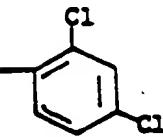
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TABLE 1 (cont)

<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p. °C</u>
5 24		CO <sub>2</sub> H		168-172
10 25		CO <sub>2</sub> Na <sup>+</sup>		>280
15 26		CO <sub>2</sub> H		183-186
20 27		CO <sub>2</sub> H		205-207
25 28		CO <sub>2</sub> H		156-162
29		CO <sub>2</sub> H		194-195
30 30		CO <sub>2</sub> Na <sup>+</sup>		>280

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TABLE 1 (cont)

<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p.°C</u>
5 31		CO <sub>2</sub> H		233-237
10 32		CO <sub>2</sub> Na <sup>+</sup>		>280
15 33		CO <sub>2</sub> H		212-216
20 34		CO <sub>2</sub> H		170-172
25 35		CO <sub>2</sub> H		
30 36		CO <sub>2</sub> H		75 (decomp.)
37		CO <sub>2</sub> H		115

-20-

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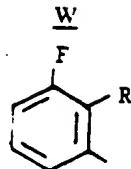
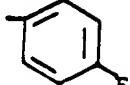
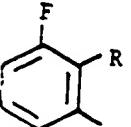
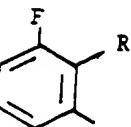
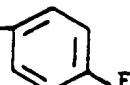
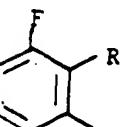
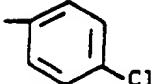
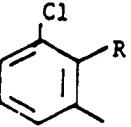
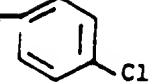
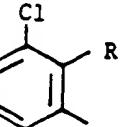
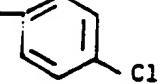
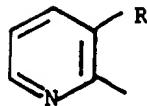
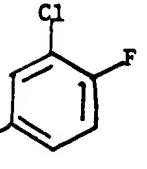
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5 38		CO <sub>2</sub> H		169.5-175.5
39		CO <sub>2</sub> H		85-93
10 40		CO <sub>2</sub> H		205-212
15 41		CO <sub>2</sub> H		
20 42		CO <sub>2</sub> H		
25 43		CO <sub>2</sub> H		
44		CO <sub>2</sub> H		
30 45		CO <sub>2</sub> H		

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TABLE 1 (cont)

<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p. °C</u>
46 5		CO <sub>2</sub> H		
47		CO <sub>2</sub> H		
10 48		CO <sub>2</sub> H		
15 49		CO <sub>2</sub> Na <sup>+</sup>		
20 50		CO <sub>2</sub> H		
25 51		CO <sub>2</sub> H		
52		CO <sub>2</sub> H		
30 53		CO <sub>2</sub> H		218-221

TABLE 1 (cont)

<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p. °C</u>
5 54		CO <sub>2</sub> Na <sup>+</sup>		>300
10 55		CO <sub>2</sub> Na <sup>+</sup>		>300
15 56		CO <sub>2</sub> H		154-167
20 57		CO <sub>2</sub> H		213-214
25 58		CO <sub>2</sub> H		169-173
30 59		CO <sub>2</sub> Na <sup>+</sup>		>300
30 60		CO <sub>2</sub> Na <sup>+</sup>		210-217

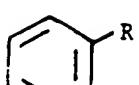
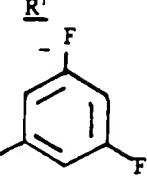
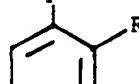
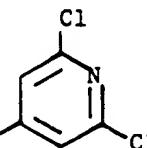
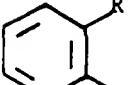
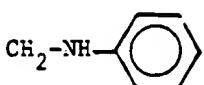
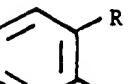
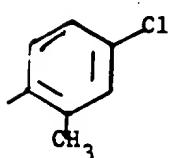
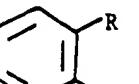
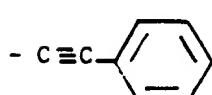
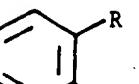
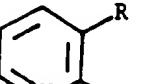
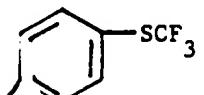
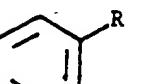
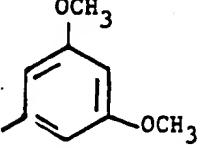
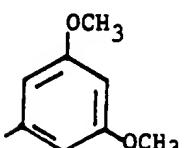
-23-

**TABLE 1 (cont)**

<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p.°C</u>
5 61		CO <sub>2</sub> H		127-134
62		CO <sub>2</sub> H		118-127
10				
63		CO <sub>2</sub> Na <sup>+</sup>		>300
15 64		CO <sub>2</sub> Na <sup>+</sup>		>300
20 25 65		CO <sub>2</sub> Na <sup>+</sup>		185-195
66		CO <sub>2</sub> Na <sup>+</sup>		>300
30 67		CO <sub>2</sub> H		238-240

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TABLE 1 (cont)

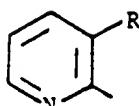
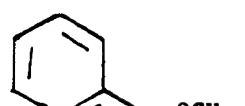
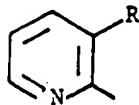
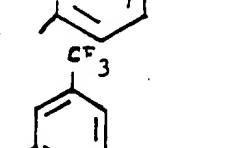
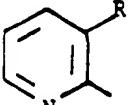
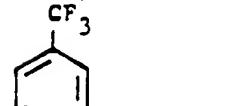
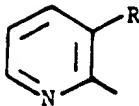
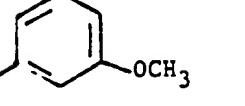
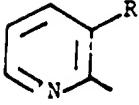
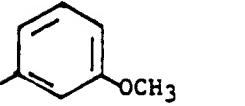
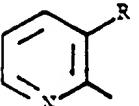
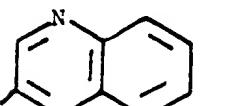
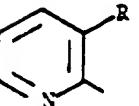
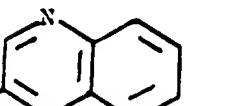
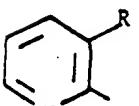
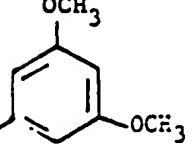
Cpd #	<u>W</u>	<u>R</u>	<u>R'</u>	m.p. °C
5 68		$\text{CO}_2\text{Na}^+$		>260
10 69		$\text{CO}_2\text{Na}^+$		176 (decomp)
15 70		$\text{CO}_2\text{Na}^+$		>250
20 71		$\text{CO}_2\text{Na}^+$		267.50 (decomp)
25 72		$\text{CO}_2\text{Na}^+$		
30 73		$\text{CO}_2\text{H}$		210-215
35 74		$\text{CO}_2\text{Na}^+$		>290
75		$\text{CO}_2\text{H}$		90-92
76		$\text{CO}_2\text{Na}^+$		>250

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TABLE 1 (cont)

Cpd #	W	R	<u>m.p. °C</u>
5 77		CO <sub>2</sub> H	138-140
10 78		CO <sub>2</sub> Na <sup>+</sup>	210-212
15 79		CO <sub>2</sub> H	243.5-247
15 80		CO <sub>2</sub> Na <sup>+</sup>	>300
20 81		CO <sub>2</sub> H	107-110
25 82		CO <sub>2</sub> Na <sup>+</sup>	>300
30 83		CO <sub>2</sub> Na <sup>+</sup>	>300
35 84		CO <sub>2</sub> H	138-141

**TABLE 1 (cont)**

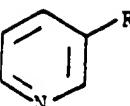
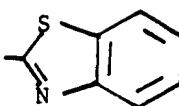
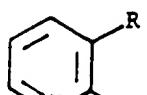
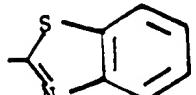
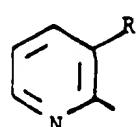
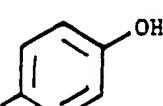
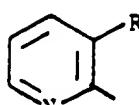
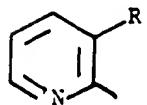
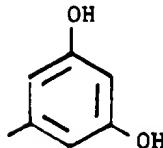
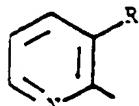
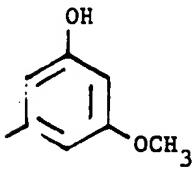
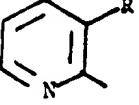
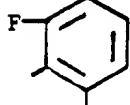
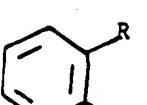
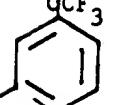
<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p. °C</u>
5 85		CO <sub>2</sub> Na <sup>+</sup>		>300
86		CO <sub>2</sub> H		180-182
10 87		CO <sub>2</sub> Na <sup>+</sup>		>300
15 88		CO <sub>2</sub> H		95-98
20 89		CO <sub>2</sub> Na <sup>+</sup>		250-252
25 90		CO <sub>2</sub> H		131-133
30 91		CO <sub>2</sub> Na <sup>+</sup>		>300
35 92		CO <sub>2</sub> H		264.5-271

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TABLE 1 (cont)

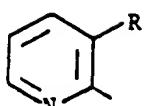
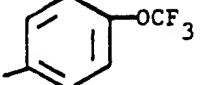
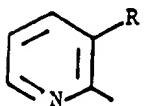
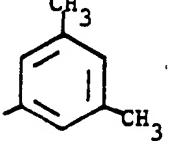
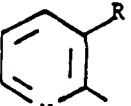
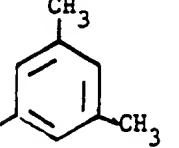
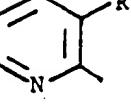
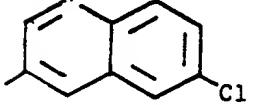
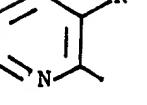
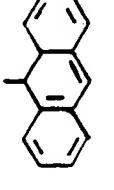
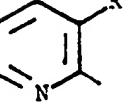
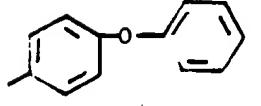
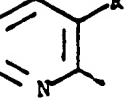
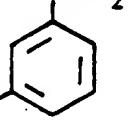
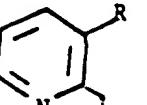
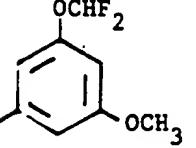
<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p. °C</u>
5 93		$\text{CO}_2\text{Na}^+$		>300
10 94		$\text{CO}_2\text{H}$		95-97
15 95		$\text{CO}_2\text{Na}^+$		222-225
20 96		$\text{CO}_2\text{H}$	$-\text{CH}_2-\text{S}-\text{C}_6\text{H}_4-\text{Cl}$	86.5-91.5
25 97		$\text{CO}_2\text{Na}^+$	$-\text{CH}_2-\text{S}-\text{C}_6\text{H}_4-\text{Cl}$	288.5-291.5
30 98		$\text{CO}_2\text{H}$		211-213
30 99		$\text{CO}_2\text{Na}^+$		>300
30 100		$\text{CO}_2\text{H}$	$-\text{CH}_2-\text{S}-\text{C}_6\text{H}_5$	oil

TABLE 1 (cont)

<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p.°C</u>
5 101		CO <sub>2</sub> H		269-270
10 102		CO <sub>2</sub> Na <sup>+</sup>		>300
15 103		CO <sub>2</sub> Na <sup>+</sup>		>275
20 104		CO <sub>2</sub> Na <sup>+</sup>		>290
25 105		CO <sub>2</sub> Na <sup>+</sup>		>300
30 106		CO <sub>2</sub> Na <sup>+</sup>		>300
35 107		CO <sub>2</sub> Na <sup>+</sup>		235
		CO <sub>2</sub> Na <sup>+</sup>		278-281

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**TABLE 1 (cont)**

<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p. °C</u>
5 109		$\text{CO}_2\text{Na}^+$		>290
10 110		$\text{CO}_2\text{H}$		209.5-213.5
10 111		$\text{CO}_2\text{Na}^+$		>300
15 112		$\text{CO}_2\text{Na}^+$		>300
20 113		$\text{CO}_2\text{Na}^+$		233-236
25 114		$\text{CO}_2\text{Na}^+$		> 300
30 115		$\text{CO}_2\text{Na}^+$		115-119
35 116		$\text{CO}_2\text{Na}^+$		244 (decomp)

-30-

TABLE 1 (cont)

<u>Cpd #</u>	<u>W</u>	<u>R</u>	<u>R'</u>	<u>m.p. °C</u>
5 117		CO <sub>2</sub> Na <sup>+</sup>		278.5-281
10 118		CO <sub>2</sub> Na <sup>+</sup>		>250
119		CO <sub>2</sub> Na <sup>+</sup>		>250
15 120		CO <sub>2</sub> Na <sup>+</sup>		>290

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TABLE 2

	<u>Cpd #</u>	<u>R</u>	<u>R<sup>2</sup></u>	<u>R<sup>1</sup></u>	<u>m.p. °C</u>
10	121	CO <sub>2</sub> Na <sup>+</sup>	OH		
15	122	CO <sub>2</sub> Na <sup>+</sup>	-CO <sub>2</sub> Na <sup>+</sup>		
	123	CO <sub>2</sub> Na <sup>+</sup>	-OC <sub>2</sub> H <sub>5</sub>		
20	124	CO <sub>2</sub> Na <sup>+</sup>	OCH <sub>3</sub>		
25	125	CO <sub>2</sub> Na <sup>+</sup>	-OC <sub>2</sub> H <sub>5</sub>		

EXAMPLE 8

The test compounds are weighed and dissolved in a stock solution consisting of acetone:deionized water (1:1) and 0.5% adjuvant mixture. Dilutions from this stock solution are performed to allow for preparation of spray solutions consisting of single 5 doses applied at a level equivalent to either 4.0, 1.0 or 0.25 kg/ha of active ingredient. The solutions are applied by a linear track sprayer set to deliver 1000 L/ha spray volume.

In pre-emergent studies, each dose of herbicide is applied as a band treatment over the seed zone. Pots containing the seeds are then top-dressed with soil, the plants are 10 grown in the greenhouse and visually evaluated 7 and 19 days after treatment.

In post-emergence studies, each dose of compound is applied to the foliage of the selected weed seedling species. The plants are allowed to grow in the greenhouse and visually evaluated at 1, 7 and 19 days after treatment. Weed species tested are shown in 15 Table 3. Some compounds of formula I showed activity in the pre-emergent and post emergent studies. Herbicidal control is evaluated as % injury with 100% injury considered complete control. At an application rate of 1.0 kg/ha active ingredient the compounds 1, 3, 5, 7-12, and 19-24 exhibited herbicidal control at greater than 80% for various tested weeds in both pre-emergence and post-emergence screenings.

20

In pre-emergence screening on grasses the compounds 60-65, 68, 71-78, 83, 84 and 94 provided greater than 75% control at 1.0 kg/ha on all tested weed species. It is understood that this list does not reflect all obtained data nor encompass all compounds which achieved the given limit.

25

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TABLE 3

	Common Name	Genus Species
5	Velvetleaf	<u>Abutilon theophrasti</u>
	Redroot Pigweed	<u>Amaranthus retroflexus</u>
	Mustard White	<u>Sinapis alba</u>
	Black Nightshade	<u>Solanum nigrum</u>
10	Wild Oat	<u>Avena fatua</u>
	Downy Brome	<u>Bromus tectorum</u>
	Barnyardgrass	<u>Echinochloa crus-galli</u>
	Green Foxtail	<u>Setaria viridis</u>

### METHODS OF APPLICATION

Application of a compound of formula I is made according to conventional procedure to the weeds or their locus using a herbicidally effective amount of the  
5 compound, usually from 1 g to 10 kg/ha.

Compounds according to the invention may be used for the control of both broadleaf and grassy weeds in both preplant incorporation and pre- and post-emergent application. Compounds may also exhibit selectivity in various crops and may thus be  
10 suited for use in weed control in crops such as but not limited to corn, cotton, wheat, soybean and rice.

The optimum usage of a compound of formula I is readily determined by one of ordinary skill in the art using routine testing such as greenhouse testing and small plot  
15 field testing. It will depend on the compound employed, the desired effect (a phytotoxic effect requiring a higher rate than a plant growth regulating effect), the conditions of treatment and the like. In general, satisfactory phytotoxic effects are obtained when the compound of formula I is applied at a rate in the range of from 0.001 to 5.0 kg, more preferably of from 0.05 to 2.5 kg per hectare, especially 0.01 to 2.5 kg per hectare.  
20

The compounds of formula I may be advantageously combined with other herbicides for broad spectrum weed control. Examples of herbicides which can be combined with a compound of the present invention include those selected from carbamates, thiocarbamates, chloroacetamides, triazines, dinitroanilines, benzoic acids,  
25 glycerol ethers, pyridazinones, uracils, phenoxy's and ureas for controlling a broad spectrum of weeds.

The compounds of formula I are conveniently employed as herbicidal compositions in association with agriculturally acceptable diluents. Such compositions also form part of  
30 the present invention. They may contain, aside from a compound of formula I as active agent, other active agents, such as herbicides or compounds having antidotal, fungicidal,

insecticidal or insect attractant activity. They may be employed in either solid or liquid forms such as a wettable powder, an emulsifiable concentrate, a granule or a microcapsule incorporating conventional diluents. Such compositions may be produced in conventional manner, for example by mixing the active ingredient with a diluent and optionally other 5 formulating ingredients such as surfactants.

Agriculturally acceptable additives may be employed in herbicidal compositions to improve the performance of the active ingredient and to reduce foaming, caking and corrosion, for example.

10

The term "diluent" as used herein means any liquid or solid agriculturally acceptable material which may be added to the active constituent to bring it in an easier or improved applicable form, respectively, to a usable or desirable strength of activity. It can for example be talc, kaolin, diatomaceous earth, xylene or water.

15

"Surfactant" as used herein means an agriculturally acceptable material which imparts emulsifiability, spreading, wetting, dispersibility or other surface-modifying properties. Examples of surfactants are sodium lignin sulfonate and lauryl sulfate.

20

Particularly formulations to be applied in spraying forms such as water dispersible concentrates or wettable powders may contain surfactants such as wetting and dispersing agents, for example the condensation product of formaldehyde with naphthylene sulphonate, an ethoxylated alkylphenol and an ethoxylated fatty alcohol.

25

In general, the formulations include from 0.01 to 99% by weight of active agent and from 0 to 20% by weight of agriculturally acceptable surfactant, and from 0.1 to 99.99% of solid or liquid diluent(s) the active agent consisting either of at least one compound of formula I or mixtures thereof with other active agents. Concentrate forms of compositions generally contain between about 2 and 95%, preferably between about 10 30 and 90% by weight of active agent.

Typical herbicidal compositions, according to this invention, are illustrated by the following Examples A, B, C, D and E in which the quantities are in parts by weight.

### EXAMPLE A

#### 5    Preparation of a Soluble Powder

The water soluble salts of this invention can be hammer milled to a screen size of 100 mesh. The resulting powder will readily dissolve in water for spraying.

### EXAMPLE B

#### 10    Preparation of a Wettable Powder

25 Parts of a compound according to this invention are mixed and milled with 25 parts of synthetic fine silica, 2 parts of sodium lauryl sulphate, 3 parts of sodium lignosulfonate and 45 parts of finely divided kaolin until the mean particle size is about 5 micron. The resulting wettable powder is diluted with water to a desired concentration.

15

### EXAMPLE C

#### Preparation of Water Dispersible Granule

40 Parts of a water insoluble parent acid compound according to this invention are wet milled in a solution of 10 parts MARASPERSE N-22 (a sodium lignosulfonate) and 20 50 parts water until a median particle size of 5 micron is reached. The slurry is spray dried on a NIRRO MOBILE MINOR unit at an inlet temperature of 150°C and outlet temperature of 70°C. The resulting granule can be readily dispersed in water for application.

#### 25    EXAMPLE D

##### Preparation of a Microcapsule Suspension

(a)    0.38 Parts of a VINOL 205 (a partially hydrolyzed polyvinyl alcohol) are dissolved in 79.34 parts water.

30    (b)    3.75 Parts of an organic soluble parent acid compound according to this invention are dissolved in 3.75 parts TENNECO 500-100 (a xylene range aromatic solvent). To this

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solution are added 0.63 parts of SEBACOYL CHLORIDE and 0.88 parts PAPI 135 (polymethylene isocyanate).

(c) 1.89 Parts piperazine and 0.50 parts of NaOH are dissolved in 12.60 parts of water.

5

Transfer premix (a) to a one quart osterizer and while stirring add premix (b) and sheer for approximately 60 seconds or until a droplet size of 10-20 microns is reached. Immediately add premix (c), continue stirring for 3 hours and neutralize with acetic acid. The resulting capsule suspension may be diluted in water for spraying.

10

#### EXAMPLE E

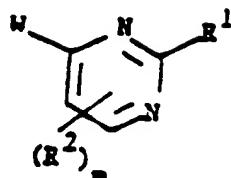
##### Preparation of an Emulsifiable Concentrate

13 Parts of an organic soluble parent acid compound according to this invention are dissolved in 79 parts of TENNECO 500-100 along with 2 parts TOXIMUL RHF and 6  
15 parts TOXIMUL S. TOXIMULS are a "matched pair"; each containing anionic and nonionic emulsifiers. The stable solution will spontaneously emulsify in water for spraying.

WHAT IS CLAIMED IS:

1. A compound of the formula

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10 wherein W is a substituted phenyl or a substituted 5- or 6-membered aromatic heterocyclic ring wherein one or two atoms of said ring are selected from oxygen, nitrogen and sulfur; W being substituted by at least R;

15

R is  $\text{CO}_2\text{R}^4$ ,  $\text{CHO}$ ,  $\text{CONH-O-CH}_2\text{CO}_2\text{R}^4$ ,  $\text{COSR}^4$ ,  $\text{CO}_2\text{CHR}^5\text{OCOR}^6$  or  $\text{CH=NOR}^4$ ;

15

15 R<sup>1</sup> is Ar, (Z)<sub>x</sub>Y-Ar, and ZAr wherein Ar is an optionally substituted aryl or heteroaryl group selected from the group consisting of phenyl, pyridyl, piperonyl, naphthyl, indolyl, quinolyl, isoquinolyl, quinoxalinyl, quinazolinyl, benzoxazolyl, benzothiazolyl, phenanthryl, pyridyl-N-oxide, anthranilyl, pyrimidinyl, pyrazinyl, thienyl, furyl, pyrrolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, imidazolyl, pyrazolyl, oxadiazolyl and thiadiazolyl; wherein the optional substituents are phenoxy, halo, alkyl, alkenyl, haloalkyl, haloalkylthio, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, haloalkoxy, alkoxyalkyl, cyano, nitro, alkoxy carbonyl, amino, alkylamino, dialkylamino or hydroxy; Y is O, S or NH; Z is optionally substituted C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>2</sub>-C<sub>4</sub>alkynyl, or an optionally substituted C<sub>2</sub>-C<sub>4</sub>alkenyl, wherein the substituents are independently alkyl and halogen;

20

25

x is 0 to 2;

20

25

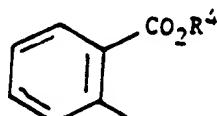
R<sup>2</sup> is independently hydrogen, halogen, alkyl, alkenyl, haloalkyl, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, alkoxyalkyl, cyano, nitro, amino, alkylamino, dialkylamino,  $\text{CO}_2\text{R}^4$  or hydroxy;

m is 1 to 2;

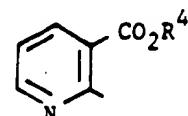
R<sup>4</sup> is hydrogen, alkali or alkaline earth cation, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium cation, trialkylsulfoxonium cation, alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl or optionally substituted phenylalkyl;

R<sup>5</sup> is hydrogen or alkyl; and

10 R<sup>6</sup> is alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl or optionally substituted phenylalkyl and provided that (i) when R<sup>1</sup> is phenyl; W is not



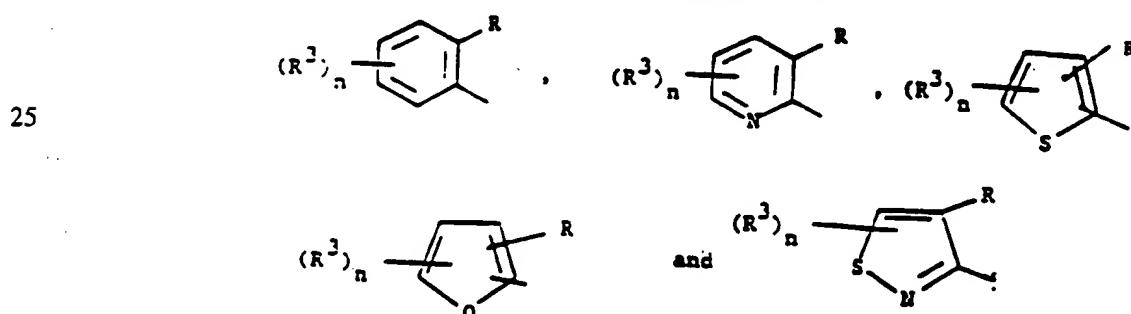
15 and (ii) when R<sup>1</sup> is optionally substituted phenyl and W is



R<sup>2</sup> is not alkyl or alkenyl.

2. A compound according to Claim 1 wherein W is phenyl, pyridyl, thienyl, 20 furyl or isothiazolyl.

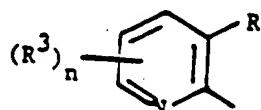
3. A compound according to Claim 2 wherein W is



30 wherein R<sup>3</sup> is independently hydrogen, halogen, alkyl, haloalkyl, alkoxy, cyano, alkoxy-carbonyl, alkylamino, dialkylamino, and -N(R<sup>5</sup>)-CO-R<sup>6</sup>, and n is 1 to 4.

-40-

4. A compound according to Claim 3 wherein W is



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R is CO<sub>2</sub>R<sup>4</sup>; CHO; CONH-O-CH<sub>2</sub>CO<sub>2</sub>R<sup>4</sup>; COSR<sup>4</sup>; CO<sub>2</sub>CHR<sup>5</sup>OCOR<sup>6</sup> or CH=NOR<sup>4</sup>;

R<sup>1</sup> is Ar, Z<sub>x</sub>YAr or ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl, anthranilyl or 10 phenanthryl;

R<sup>2</sup> is hydrogen, CO<sub>2</sub>R<sup>4</sup> and alkoxy; and

R<sup>3</sup> is hydrogen and halogen.

15

5. A compound according to Claim 4 wherein R is CO<sub>2</sub>CHR<sup>5</sup>OCOR<sup>6</sup> or CO<sub>2</sub>R<sup>4</sup>; R<sup>4</sup> is hydrogen, Na, NH<sub>4</sub>, K, Ca, Mg, trimethylsulfonium, trimethyl sulfoxonium and isopropylammonium, R<sup>1</sup> is optionally substituted phenyl, pyridyl, naphthyl, piperonyl, quinolyl, (Z)phenyl, or (Z)<sub>x</sub>Ophenyl; Z is C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>2</sub>-C<sub>4</sub>alkynyl or C<sub>2</sub>-C<sub>4</sub>alkenyl and x 20 is 1.

6. A compound according to Claim 3 wherein W is



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R is CO<sub>2</sub>R<sup>4</sup>; CHO; CONH-O-CH<sub>2</sub>CO<sub>2</sub>R<sup>4</sup>; COSR<sup>4</sup>; CO<sub>2</sub>CHR<sup>5</sup>OCOR<sup>6</sup> or CH=NOR<sup>4</sup>;

30 R<sup>1</sup> is Ar, Z<sub>x</sub>YAr or ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl, anthranilyl or

phenanthryl;

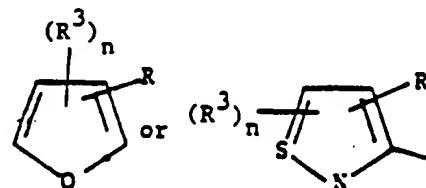
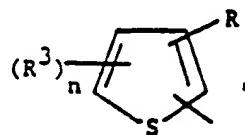
$R^2$  is hydrogen, alkyl,  $CO_2R^4$ , and, alkoxy; and

5         $R^3$  is hydrogen and halogen.

7.        A compound according to Claim 4 wherein R is  $CO_2CHR^5OCOR^6$  or  
 $CO_2R^4$ ;  $R^4$  is hydrogen, Na, NH<sub>4</sub>, K, Ca, Mg, trimethylsulfonium, trimethyl sulfoxonium  
and isopropylammonium;  $R^2$  is hydrogen and  $R^1$  is optionally substituted phenyl, pyridyl,  
10      naphthyl, piperonyl, quinolyl, (Z)phenyl, or (Z)<sub>x</sub>Ophenyl and x is 1.

8.        A compound according to Claim 3 wherein W is

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$R$  is  $CO_2R^4$ ; CHO; CONH-O-CH<sub>2</sub>CO<sub>2</sub>R<sup>4</sup>; COSR<sup>4</sup>;  $CO_2CHR^5OCOR^6$  or CH=NOR<sup>4</sup>;

20

$R^1$  is Ar, Z<sub>x</sub>OAr or ZAr wherein Ar is an optionally substituted phenyl, pyridyl,  
naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl or phenanthryl;

$R^2$  is hydrogen; and

25

$R^3$  is hydrogen and halogen.

9.        A compound according to Claim 3 wherein

$R$  is  $CO_2R^4$ ;

30

$R^4$  is hydrogen, Na, NH<sub>4</sub>, K, Ca, Mg, trimethylsulfonium, trimethylsulfoxonium or

isopropylammonium;

R<sup>1</sup> is Ar, (Z)<sub>x</sub>Y-Ar and ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl, anthranilyl or 5 phenanthryl wherein the optional substituents are halo, alkyl, alkenyl, haloalkyl, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, haloalkoxy, alkoxyalkyl, cyano, nitro, alkoxy carbonyl, amino, alkylamino, dialkylamino and hydroxy; Y is O, S or NH; Z is an optionally substituted C<sub>1</sub>-C<sub>3</sub>alkyl, C<sub>2</sub>-C<sub>4</sub>alkynyl, or an optionally substituted C<sub>2</sub>-C<sub>4</sub> alkenyl wherein the substituents are independently alkyl and halogen; and x is 0 to 2.

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10. A herbicidal composition comprising a herbicidally effective amount of a compound of Claim 1 in association with an agriculturally acceptable diluent.

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## INTERNATIONAL SEARCH REPORT

Intern. Application No  
PCT/EP 95/00086

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 C07D401/04 A01N43/54 C07D401/14 C07D405/04 C07D239/24  
 C07D417/04 C07D409/04 C07D405/14 C07D417/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 6 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 752 324 (THOMAS) 21 June 1988 cited in the application see claim 1 ---	1-10
X	BIOCHEM. INT., vol. 1982, 1982 pages 431-438, PRYOR ET AL 'Purification of maize alcohol dehydrogenase and competitive inhibition by pyrazoles.' Compound 20 on page 435 ---	1-10 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

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- \*'P' document published prior to the international filing date but later than the priority date claimed

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2

Date of the actual completion of the international search

30 May 1995

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 95/00086

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AUST J.CHEM., vol. 32, 1979 pages 669-679, HARRIS ET AL 'Synthetic Plant Growth Regulators' cited in the application Compound 4 on page 669 ---	1-10
X	DE,A,40 31 798 (HOECHST) 9 April 1992 cited in the application see claim 1 ---	1-10
A	EP,A,0 484 750 (BAYER AG) 13 May 1992 see claim 1 -----	1-10

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/EP 95/00086

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4752324	21-06-88	DE-A-	3623302	14-05-87
		EP-A-	0222254	20-05-87
		JP-A-	62120382	01-06-87
DE-A-4031798	09-04-92	NONE		
EP-A-484750	13-05-92	DE-A-	4035141	07-05-92
		JP-A-	4283578	08-10-92